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16. ABSTRACT

The fate of 14 polycyclic aromatic hydrocarbon (PAH) compounds was evaluated with regard to interphase transfer potential and mechanisms of treatment in soil under unsaturated conditions. Volatilization and abiotic and biotic fate of the PAHs were determined using two soils not previously exposed to these compounds. Volatilization accounted for approximately 30 and 20% loss of naphthalene and 1-methylnaphthalene, respectively; for the remaining compounds, volatilization was negligible. Abiotic reactions accounted for approximately 2 to 20% of the reduction in concentration in solvent extracts for two- and three-ring PAH compounds; no statistically significant reduction was observed for PAH compounds containing greater than three aromatic rings. Biotic mechanisms were quantified as first-order rate constants corrected for volatilization and abiotic mechanisms. Half-life values increased from approximately 2 to 60 to more than 300 d for two-, three- and four- and five- ring PAH compounds, respectively. In general, biological degradation rates were not significantly different between the two soils. Information concerning interphase transfer potential and mechanisms of treatment provides the basis for a rational approach to remediation of soil contaminated with PAH compounds.

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Environmental Chemistry

FATE OF PAH COMPOUNDS IN TWO SOIL TYPES: INFLUENCE OF VOLATILIZATION, ABIOTIC LOSS AND BIOLOGICAL ACTIVITY

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Abstract—The fate of 14 polycyclic aromatic hydrocarbon (PAH) compounds was evaluated with regard to interphase transfer potential and mechanisms of treatment in soil under unsaturated conditions. Volatilization and abiotic and biotic fate of the PAHs were determined using two soils not previously exposed to these compounds. Volatilization accounted for approximately 30 and 20% loss of naphthalene and 1-methylnaphthalene, respectively; for the remaining compounds, volatilization was negligible. Abiotic reactions accounted for approximately 2 to 20% of the reduction in concentration in solvent extracts for two- and three-ring PAH compounds; no statistically significant reduction was observed for PAH compounds containing greater than three aromatic rings. Biotic mechanisms were quantified as first-order rate constants corrected for volatilization and abiotic mechanisms. Half-life values increased from approximately 2 to 60 to more than 300 d for two-, three- and four- and five-ring PAH compounds, respectively. In general, biological degradation rates were not significantly different between the two soils. Information concerning interphase transfer potential and mechanisms of treatment provides the basis for a rational approach to remediation of soil contaminated with PAH compounds.

Keywords—Soil Degradation Volatilization Abiotic loss Biotic loss

INTRODUCTION

Polynuclear aromatic hydrocarbons (PAHs) include a group of organic pollutants of critical public health and environmental concern due to the following characteristics: (a) chronic health effects and carcinogenicity, (b) microbial recalcitrance, (c) high bioaccumulation potential and (d) low removal efficiency in traditional wastewater treatment processes [1]. PAHs have been identified in soils and groundwater at a wide range of uncontrolled disposal sites, including wood petroleum, oily wastes and coal gasification sites [2,3].

Treatment of PAH-contaminated soil has frequently been reported in terms of the decrease in the soil concentration of a parent PAH compound with increasing time of incubation in the soil [3–9]. Typically, soil samples are taken from a field site or a laboratory microcosm and extracted with a solvent. The concentration of PAH compound is usually measured in the solvent extract of the soil using gas or liquid chromatography. The change in concentration of PAH compound in the solvent with time is often used to calculate a rate of decrease in the concentration of the PAH compound in soil. Rate information can be used to determine important engineering and management factors concerning soil decontamination, including: (a) the time required to decrease the concentration to one-half of the original concentration (half-life), (b) the time required to attain cleanup targets for a soil and (c) the effects of environmental factors, such as temperature and moisture, on the rate of decrease.

Additional information concerning mechanisms and pathways by which PAH compounds are interacting with a soil environment is necessary to un-

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derstand whether a PAH compound is simply transferred from one soil phase (solid phase) to another (air phase) through a process of interphase transfer, or is chemically altered so that the properties of the parent compound are changed. Although PAH compounds have been shown to be biologically degraded in controlled laboratory conditions in pure and mixed liquid cultures, the rate and extent to which PAH compounds are biologically degraded in the multiphase system of the soil environment have not been well characterized [8,10–12]. Evaluation of the fate of a PAH compound in soil requires identification and measurement of distribution among the physical phases that comprise a soil system, as well as differentiation of the mechanisms by which a PAH compound may be chemically altered in a soil system [8,13–15].

Enhancing the information obtained concerning rate of apparent loss of PAH compounds from a soil extract with information concerning interphase transfer potential between solid and gas phases of soil and mechanisms of interaction of PAH compounds with soil phases will provide the basis for a more rational approach to bioremediation of sites contaminated with PAH compounds. Remediation alternatives can be based upon specific media (soil, air) and upon specific mechanisms, including recovery of air phase, enhancement of abiotic destruction or enhancement of biological degradation, to enhance treatment [16]. Evaluation of interphase transfer also allows characterization of routes by which PAHs may migrate from the soil to the multimedia environment that lead to human exposure. This information is valuable in the determination of risk and implementation of risk management strategies.

The objectives of this research were to evaluate two soil types with regard to: (a) interphase transfer potential and (b) mechanisms of interaction for 14 PAH compounds. Specifically, volatilization and abiotic and biotic mechanisms of PAH compounds were determined using two soils not previously exposed to these compounds.

MATERIALS AND METHODS

Soil

Two soil types used in this study were a Kidman sandy loam (Calciaquoll; Utah) and a McLaurin sandy loam soil (Paleudult; Mississippi). Soils were collected from the surface to a depth of 0.15 m. The collected soils were air-dried and sieved to pass a 2-mm screen. Properties of the soils are presented in Table 1; information concerning the procedures and analyses used to characterize the soils is presented elsewhere [8,14].

PAHs

The 14 PAH compounds evaluated in this study included: naphthalene, 1-methylnaphthalene, anthracene, phenanthrene, fluoranthene, chrysene, pyrene, benz[*a*]anthracene, 7,12-dimethylbenzanthracene, benzo[*a*]pyrene, dibenz[*a*,*h*]anthracene (Aldrich Chemical Co. Inc., Milwaukee, WI), benzo[*b*]fluoranthene, indeno[1,2,3-*cd*]pyrene (The Foxboro Co., North Haven, CT) and dibenzo[*a*,*i*]-pyrene (Sigma Chemical Co., St. Louis, MO). These PAHs were selected based on: (a) presence of these compounds in industrial wastes that are commonly treated in soil systems [2,3,7,8], (b) lack of information concerning mechanisms of PAH interaction in unsaturated soil systems [3,9,14] and (c) public health and environmental significance [1,8]. These PAH compounds were evaluated individually in both soils at concentrations representative of full-scale uncontrolled waste disposal sites and land treatment units [2,8,13,14].

Experimental apparatus

Interphase transfer and treatment mechanisms were measured using the experimental apparatus shown in Figure 1 [7,8]. The apparatus consisted of: (a) an Erlenmeyer flask (500 ml) with a fitted glass aeration cap (volatilization flask units), (b)

Table 1. Characteristics of soils used in this study

Soil	pH	Organic carbon (%)	EC (dS/m)	CEC (meq/100 g)	Moisture (−1/3 bar)	Soil plate counts (cfu/g soil)	
						Bacteria	Fungi
Kidman sandy loam	7.9	0.5	0.2	10.1	16.3	6.7E6	1.9E4
McLaurin sandy loam	4.8	1.1	0.09	4.4	12.4	1.1E5	5.3E4

EC, electrical conductivity; CEC, cation exchange capacity; cfu, colony-forming units.

of 24 d. The biological degradation rates of PAH compounds were not statistically different between the Kidman and McLaurin soils (Tables 5 and 6).

CONCLUSIONS

Information concerning interphase transfer potential between solid and gas phases in soil and mechanisms of removal of PAH compounds in unsaturated soil systems that contain solid, liquid and gas phases can provide valuable information for determining which soil processes are most important in affecting the behavior and fate of these compounds at a contaminated waste site. If compounds are transferred to the soil air phase, recovery of the air phase, e.g., through vacuum extraction or through flexible air inflatable domes, and treatment of the air phase may be appropriate. If compounds are destroyed through abiotic processes, abiotic degradation may be accomplished through addition of chemicals or changes in soil chemical and physical properties without the need to take into consideration those parameters that may adversely affect soil microorganisms. If biological mechanisms are predominant in influencing the fate of compounds in soil systems, an approach based upon identification and management of biologically sensitive parameters under site- and soil-specific conditions should be emphasized.

Results obtained in this study indicate that interphase transfer potential appears to be potentially significant for two-ring PAH compounds in a multiphase soil system. Destruction mechanisms including abiotic and biotic processes appear to be important in influencing the fate of PAH compounds in soils where photodegradation is controlled. Abiotic mechanisms appear to be potentially important for two- and three-ring PAH compounds, while for PAH compounds with greater than three rings neither volatilization nor abiotic mechanisms played a significant role in determining behavior. For PAH compounds with greater than three aromatic rings, biological degradation appears to influence the fate of these compounds in a multiphase soil system. These results indicate that strategies to augment the biodegradation reaction in soil systems may allow faster degradation of high molecular weight PAH compounds, resulting in the reduction or elimination of mass transport of PAH compounds through the vadose zone and into the groundwater at a contaminated waste site. Approaches to augmenting biological activity to accelerate the destruction of PAH compounds have been characterized and evaluated, and include temperature, moisture, addition of nonhazardous organic matter and the management of cooxidation processes in soil [5,7, 14–16,20].

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REFERENCES

1. **Herbes, S.E., G.R. Southworth** and **C.W. Ghers.** 1976. Organic contamination in aqueous coal conversion effluents: Environmental consequences and research priorities. In D.D. Hemphill, ed., *Proceedings*, Trace Substances in the Environment. University of Missouri, Columbia, MO. April 20–24.
2. **Mahmood, R.J.** 1989. Enhanced mobility of polynuclear aromatic hydrocarbons in unsaturated soil. Ph.D. thesis. Department of Civil and Environmental Engineering, Utah State University, Logan, UT.
3. **Sims, R.C.** and **M.R. Overcash.** 1983. Fate of polynuclear aromatic compounds in soil-plant systems. *Residue Rev.* **88**:1–68.
4. **Bossert, L., W.M. Kachel** and **R. Bartha.** 1984. Fate of hydrocarbons during oily sludge disposal in soil. *Appl. Environ. Microbiol.* **47**:764–767.
5. **Coover, M.P.** and **R.C. Sims.** 1987. The rate of benzo[*a*]pyrene degradation in a manure amended sandy loam soil. *Haz. Waste Haz. Materials* **4**:151–158.
6. **Coover, M.P., R.C. Sims** and **W.J. Doucette.** 1987. Extraction of polycyclic aromatic hydrocarbons from spiked soil. *J. Assoc. Off. Anal. Chem.* **70**:1018–1020.
7. **U.S Environmental Protection Agency.** 1986. Permit guidance manual on hazardous waste land treatment demonstrations. EPA 530-SW86-032. Office of Solid Waste, Washington, DC.
8. **U.S. Environmental Protection Agency.** 1986. Waste/soil treatability studies for four complex industrial wastes: Methodologies and results. EPA 600/6-86-003a,b. Office of Research and Development, Robert S. Kerr Environmental Research Laboratory, Ada, OK.
9. **Bulman, T.S., S. Lesage, P.J.A. Fowlie** and **M.D. Weber.** 1985. The persistance of polynuclear aromatic hydrocarbons in soil. A report prepared for the Petroleum Association for Conservation of the Canadian Environment (PACE) Report No. 85-2. Environment Canada, Wastewater Technology Centre, Burlington, Ontario, Canada.
10. **Davies, J.L.** and **W.C. Evans.** 1964. Oxidative metabolism of naphthalene by soil pseudomonads. *Biochem.* **91**:251–261.
11. **Dean-Raymond, D.** and **R. Bartha.** 1975. Biodegradation of some polynuclear petroleum components by marine bacteria. *Dev. Ind. Microbiol.* **16**:97–110.
12. **Evans, W.C., H.N. Fernley** and **E. Griffiths.** 1965. Oxidative metabolism of phenanthrene and anthracene by soil pseudomonads: The ring fission mechanism. *Biochem. J.* **95**:819–821.